

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements relating to Flame Spraying

We, METCO INC., a corporation organized under the laws of the State of New Jersey, United States of America, of 1101, Prospect Avenue, Westbury, Long Island, New York, United States of America, hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the flame spraying of metallics and is a modification of that of our Patent Specification 1,000,353 to which reference can be made for general description of the state of the art, of the method of working, of the blast gas, and of powder particles sizes and methods of preparation.

The invention provides a flame spray powder in the form of individual nucleus particles coated with a coating layer of a finely divided powder bound to the nucleus by a binder, the finely divided powder of the coating layer being of a material differing from said nucleus and exothermically reactive therewith when melted together forming an intermetallic compound with the release of at least 3000 gram calories per gram atom. The term "gram calories" is used herein for the avoidance of doubt to indicate the amount of heat necessary to raise the temperature of one gram of water through 1 degree C.

The invention includes a flame spray process in which a flame spray powder according to the invention is heated in a heating zone to at least heat-softened condition and propelled in that condition out of the zone in finely divided form.

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction releasing at least 3000 calories per gram atom, and preferably at least 7,500 calories per gram atom may be used. The term "calories

per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. The average atomic weight referred to is the sum of the atomic weight of each atom in the compound divided by the number of atoms. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, each as either the nucleus or the coating layer, it only being required that they be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with one or more of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with one or more of Ti, Nb, Cr, W, Co, Mo, Ni or Ta. While iron itself is not a satisfactory com-

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ponent, it may be present in addition to another component, which in itself is satisfactory, for example in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render it rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

Where one or more of the component metals is available as a metal hydride, it may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1—10% by weight, and preferably 1—5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules may contain other conventional flame spray components, for example boron or silicon or a mixture thereof, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic compound. In a similar manner, the aggregates may contain further flame spray components, or be mixed with flame spray powders.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of the coating layer component as a coating in the form of a paint on the nucleus component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set and dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish

solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example —325 mesh. The mesh referred to herein is invariably in U.S. Standard screen size. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powder may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between  $\frac{1}{8}$ " and 20 gauge, and are preferably of the following sizes:  $\frac{3}{8}$ "  $\pm .0005$ ",  $\frac{1}{2}$ "  $\pm .0005$ ",  $\frac{5}{8}$ "  $\pm .0005$ ",  $\frac{3}{4}$ "  $\pm .0005$ ",  $\frac{7}{8}$ "  $\pm .0005$ ",  $1\frac{1}{8}$ "  $\pm .0005$ ", and 15 gauge  $\pm .001$ ",

with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat *in situ* in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign or non-metallic element is introduced and in which undesirable components may be produced. Apart from greatly contributing to the thermal efficiency of the process, the heat generated *in situ* in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adherent coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying may be effected using conventional flame spray equipment preferably in conjunction with conventional surface preparation.

The use of the composite as, for example,

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the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20%, by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following Examples illustrate the invention:

Finely divided aluminum powder (-325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

#### EXAMPLE 1.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between -200 and

+325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to ensure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a -100 mesh powder. The end powder consisted of approximately 15 weight % aluminum and 85 weight % nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 of Patent Specification 1,000,353 producing a similar coating having, however, more than twice the tensile strength of that coating.

#### EXAMPLE 2.

The following gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention. Each of the component pairs as listed in the Table may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders and sprayed as in Example 1.

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TABLE

Ag Ce	As In	Bi Mg	In Te	Pb Pu
Al As	As Mg	Bi Na	In Ru	Pb Se
Al Au	As Zn	Bi Se	K Sb	Pb Tl
Al B	B Y	Bi Te	K Se	Pd U
Al Ba	B Ca	Bi Th	K Sn	Pr Sn
Al Ca	B Cr	Ca Pb	K Tl	Pr Tl
Al Ca	B Hf	Ca Sn	La Pb	Sb Zr
Al Co	B Nb	Ca Tl	La Sb	Se Sn
Al Cr	B Ta	Cd Li	La Sn	Se Th
Al La	B Th	Cd Na	La Tl	Se Tl
Al Li	B Ti	Ca In	La Zn	Cu Te
Al Mo	B V	Ce Mg	Li Pb	Si Ti
Al Nb	B W	Ce Pb	Li Sb	Si U
Al Ni	B Zr	Ce Si	Li Sn	Si V
Al Pr	Ba Bi	Ce Sn	Li Tl	Si Zr
Al Ti	Ba Pb	Ce Tl	Li Zn	Sn Te
Al Zr	Ba Sb	Ce Zn	Mg Sb	Sn U
Al Sb	Be Co	Ga Na	Mg Sn	Sn Zr
Al Se	Be Cr	Ga Pr	Na Pb	Te Zn
Al Ta	Be Ni	Ga Sb	Na Sb	Mo Be
Al Te	Be Np	Ga Te	Na Se	Nb Be
Al U	Be Pu	Ga U	Na Sn	Ta Be
Al V	Be U	Ge Mg	Na Te	V Be
Al W	Be Zr	Ge Nb	Na Tl	Ti Be
As Cd	Bi Ca	Ge Zr	Nb Si	Cr Si
As Ga	Bi Ce	Si W	Ni Th	Cr Ti
Co Si	Bi K	Li In	Pb Pr	Cr Zr
Mo Si	Bi Li	Ni Si		
Mg Te	Si Ta			
Ni Te				
Si Th				

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## WHAT WE CLAIM IS:—

1. A flame spray powder in the form of individual nucleus particles coated with a coating layer of a finely divided powder bound to the nucleus by a binder, the finely divided powder of the coating layer being of a material differing from said nucleus and exothermically reactive therewith when melted together forming an intermetallic compound with the release of at least 3000 gram calories per gram atom.
2. A powder according to claim 1 in which intermetallic compound is formed with the release of at least 7,500 gram calories per gram atom.
3. A powder according to claim 1 or claim 2 in which the components are a component pair listed in the Table herein before.
4. A powder according to claim 1 comprising a nucleus of nickel and a coating of finely divided aluminum particles.
5. A powder according to any of the preceding claims which contains a metal hydride.
6. A powder according to any of the preceding claims which contains boron or silicon of a mixture thereof.
7. A flame spray process in which a powder according to any of the preceding claims is heated in a heating zone to at least heat-softened condition and propelled in that condition out of the zone in finely divided form.
8. A method of manufacturing a flame spray powder according to any of claims 1 to 6 in which the coating layer component is deposited as a coating in the form of a paint on the nucleus component.
9. A method according to claim 8 in which the paint contains a binder material which does not depend on solvent evaporation in order to form a dried or set film.
10. A method according to claim 9 in which the binder contains a phenolic varnish.
11. A method of manufacturing a flame spray powder substantially as herein before described in Example 1.
12. A surface flame spray with a powder according to any of claims 1 to 6.

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